

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No. : 10/567,178 Confirmation No.: 6741
Applicant (s) : Erlind M. Thorsteinson et al.
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TC/A.U. : 4181
Examiner : Joseph Micali
Title : IMPROVED ALUMINA CARRIERS AND SILVER-BASED
CATALYSTS FOR THE PRODUCTION OF ALKYLENE OXIDES
Docket No. : 62562A
Customer No. : 00109

Declaration Under 37 C.F. R. § 1.132

The undersigned, Dr. Juliana G. Serafin, citizen of the United States of America and residing in Charleston, West Virginia, declare and say that:

1. I am a 1982 graduate of the West Virginia University, Morgantown, WV with a Bachelor of Science degree in Chemistry; a 1984 graduate of Harvard University with a Master of Arts in Chemistry; and a 1989 graduate of Harvard University with a Ph.D. in Physical Chemistry.

2. From October 1989 to August 2008, I was employed by Union Carbide Company ("UCC") in South Charleston in research and development of ethylene oxide catalysts. The positions I held included: Senior Chemist, Project Scientist, Research Scientist, and Research Leader. My responsibilities included the discovery and implementation of new ethylene oxide catalyst formulations as well as modification of catalyst carriers.

3. In the fall of 2008, I began teaching at University of Charleston as an Assistant Professor of Chemistry.

4. I am currently an inventor on one granted US patent and three US published applications in the field of ethylene oxide catalysis.

5. I have read the above referenced patent application, the Office Actions dated 10-14-2008, 2-13-2009, and 6-26-2009.

6. The following paragraphs 8 through 22 are based upon work which I conducted or requested be conducted while employed at UCC.

7. Four alpha-alumina carriers, Comparative Carriers 1, 2, 3, and 4 were prepared by a carrier manufacturer at my request using the general method described in paragraph [0032] of US 2006/0258532 A1 (the present application). The fluorided

mixture of peptized boehmite alumina and gamma-alumina have the same target formulation as Starting Carriers BB and CC of the '532 patent application, except that 1, 2 and 3 wt% of nepheline syenite (a mineral containing nepheline and feldspar) were added to the starting mixtures (i.e., prior to forming and calcining) for Comparative Carriers 2, 3 and 4, respectively.

8. Certain properties of Comparative Carriers 1, 2, 3 and 4 after calcination are set forth in Table 1.

Table 1

comparative carrier no.	nepheline syenite in mix (wt %)	surface area (m ² /g)	pore volume (cc/g)	Acid leachable Al (ppm)	total SiO ₂ (wt %)	
1	0	0.78	0.65	86	nd	
2	1	0.79	0.66	127	nd	
3	2	1.03	0.69	175	nd	
4	3	1.71	0.65	1402	0.3	

nd = not detected

9. Nepheline syenite comprises 50-56 wt% SiO₂. The data show that when this alkali silicate-containing modifier is incorporated into the mixture prior to calcination with accompanying conversion of the precursor aluminas to alpha-alumina, only a small fraction of the original silica/silicates introduced as nepheline syenite remains in the finished (pre-formed) carrier.

10. As compared to Comparative Carriers 1, 2 and 3, the substantial elevation in both surface area and acid leachable alumina of Comparative Carrier 4, which is the only carrier retaining a detectable amount of any Si-containing modifier(s) introduced as nepheline syenite into the starting mixture, demonstrates incomplete conversion of the starting aluminas into the desired alpha-alumina phase. This data supports paragraph [0032] of US 2006/0258532 A1:

Where preformed alpha-alumina carrier is used which has been prepared as described above in this paragraph, it is important that the alumina which has been peptized with an acidic mixture containing halide anions be calcined before impregnation with the at least one modifier, because the halide is necessary for forming platelets of alpha-alumina in the preformed alpha-alumina carrier. *If the halogenated alumina were impregnated with the at least one modifier without first calcining the halogenated alumina after peptizing the boehmite alumina and/or gamma-alumina, the at least one modifier would eliminate some or*

substantially all of the halide anions, which would then not be available for assisting in the formation of platelets of alpha-alumina. (emphasis added)

11. Catalysts were prepared on Comparative Carriers 1, 2 and 3 following the procedure described in paragraphs [0104] through [0108] of US 2006/0258532 A1. Two impregnations of silver-amine-oxalate solution were used for each catalyst. Cesium sulfate, cesium hydroxide, manganous nitrate and diammonium EDTA were added to the solution for the second impregnation in each case to attain the desired level of each promoter on the finished catalyst.

12. The calculated compositions (except for Na, which is analyzed) of Comparative Catalysts A-1, A-2 and A-3 are set forth in Table 2.

Table 2

comparative catalyst	comparative carrier	wt% Ag	Cs (ppm)	SO ₄ (ppm)	Mn (ppm)	analyzed Na (ppm)
A-1	1	33.8	436	122	83	<30
A-2	2	34.5	451	128	82	<30
A-3	3	33.4	565	159	105	118

13. Portions of Comparative Catalysts A-1, A-2 and A-3 were ground and sized to 30/50-mesh and 0.5-g charges were then tested in parallel microreactors as described in paragraph [0093] of the '532 patent application using the following reaction conditions: inlet feed composition of 30.0 mol% ethylene, 8.0 mol% oxygen, 6.5 mol% carbon dioxide, 0.5 mol% ethane, 3.5 ppmv ethyl chloride, balance nitrogen; reactor pressure 200 psig (1380 kPa gauge); total flow 120 cc/min. Following startup, the temperature of each micro reactor tube was adjusted to maintain 1.7 mol% outlet ethylene oxide concentration over the duration of the run.

14. The temperature and efficiency for each catalyst at 1.7 mol% outlet ethylene oxide concentration after cumulative productions of 4 and 12 thousand lbs ethylene oxide per cubic foot of catalyst (0.064 and 0.192 kT EO per m³ catalyst) and the corresponding temperature and efficiency aging rates over this period are set forth in Table 3.

Table 3.

comparative catalyst	4 Mlb/ft3		12 Mlb/ft3		T aging (°C/Mlb/ft3)	eff aging (%/Mlb/ft3)
	T (°C)	efficiency	T (°C)	efficiency		
A-1	239	82.7	246	82.3	0.9	-0.05
A-2	252	81.4	260	80.3	1.0	-0.14
A-3	253	81.4	263	80.6	1.3	-0.10

15. The results of this experiment show that in comparison to the unmodified control sample (Comparative Catalyst A-1 on Comparative Carrier 1), the catalysts supported on carriers prepared with 1 or 2 wt% nepheline syenite in the starting mixture (Comparative Catalysts A-2 and A-3 on Comparative Carriers 2 and 3, respectively) were initially 13-14°C less active and 1.3% less efficient. Furthermore, over the next 8 thousand lbs per cubic foot of cumulative EO production (0.128 kT per m3 catalyst), the temperature and particularly the efficiency aging rates for Comparative Catalysts A-2 and A-3 were substantially poorer.

16. Catalyst 7 of US 2006/0258532 A1 was prepared on Modified Carrier G, which was Starting Carrier BB after treatment with a sodium silicate solution as given in Table II of the application, while Catalyst 8 (comparative) was supported on Modified Carrier H, which corresponds to Starting Carrier CC without any further treatments.

17. With respect to carriers such as Modified Carrier G, paragraph [0040] of the application states that:

While the present invention is not constrained in any way by any particular theory, it is believed that during the calcining, the at least one alkali metal silicate and/or at least one alkaline earth metal silicate can react with the alumina surfaces, particularly in instances where there was a relatively high concentration (for example, 2 wt%) of the modifier (that is, at least one alkali metal silicate and/or at least one alkaline earth metal silicate) in the modifier impregnating solution. In the case where alpha-alumina is impregnated with sodium silicate modifier, such reacting is believed to result in the emergence of Na-Al-Si-O compounds in the alumina, for example, nepheline (NaAlSiO₄).

18. As noted above, Comparative Carriers 1, 2, 3 and 4 have the same starting components and compositions in their formulations as Starting Carriers BB and CC of the present application, except that 0-3 wt% of nepheline syenite are included in the starting mixture. Thus, Comparative Carriers 2, 3 and 4 represent materials prepared through direct incorporation into their starting mixtures of the same type of alkali (sodium) silicate species formed in Modified Carrier G via post-treatment of pre-formed alpha-alumina Starting Carrier BB with a sodium silicate solution.

19. Comparative Catalysts A-1, A-2 and A-3 were prepared on Comparative Carriers 1, 2 and 3 using the same formulation strategy and promoter compounds as Catalysts 7 and 8 on Modified Carriers G and H. Comparison with the early-life and aging behavior of Catalyst 8 and Comparative Catalyst A-1, both on unmodified pre-formed alpha-alumina supports, demonstrates the difference between the effects of the treatment of the formed carrier (Catalyst 7) and those resulting from direct incorporation of an alkali silicate in the carrier mixture prior to calcination and formation of alpha-alumina (Comparative Catalysts A-2 and A-3).

20. Figure 1 shows a plot of temperature data from Table 3 alongside the results given in Examples 7 and 8 of the '532 application. Catalyst 8 and Comparative Catalyst A-1, both on unmodified carriers, have very similar initial activity ($^{\circ}\text{C}$) and activity aging rates ($^{\circ}\text{C}/\text{Mlb EO}/\text{ft}^3$). The two different modes of alkali silicate modification both result in somewhat poorer initial operating temperatures relative to their respective unmodified counterparts. However, there is a dramatic reduction in activity aging rate demonstrated by Catalyst 7, which is not seen in either Comparative Catalyst A-2 or A-3.

21. Figure 2 shows a plot of efficiency data from Table 3 alongside the results given in Examples 7 and 8 of the '532 application. Again, relative to Catalyst 8 and Comparative Catalyst A-1, only Catalyst 7 provides a reduction in the efficiency aging rate ($\%/ \text{Mlb EO}/\text{ft}^3$), whereas Comparative Catalysts A-2 and A-3 experience an accelerated loss of efficiency with catalyst age. In contrast to the results for Catalyst 7, there is no evidence in the data for Comparative Catalysts A-2 and A-3 that their initially poorer activity and efficiency relative to Comparative Catalyst A-1 will improve with continued operation to the point where an advantage in either measure of performance is eventually observed.

22. The benefits derived from the claimed method of treating pre-formed alpha-alumina carrier with alkali silicates are not obtained when an alkali silicate containing modifier is included in the initial carrier formulation itself.

Figure 1 - comparison of temperature aging rates

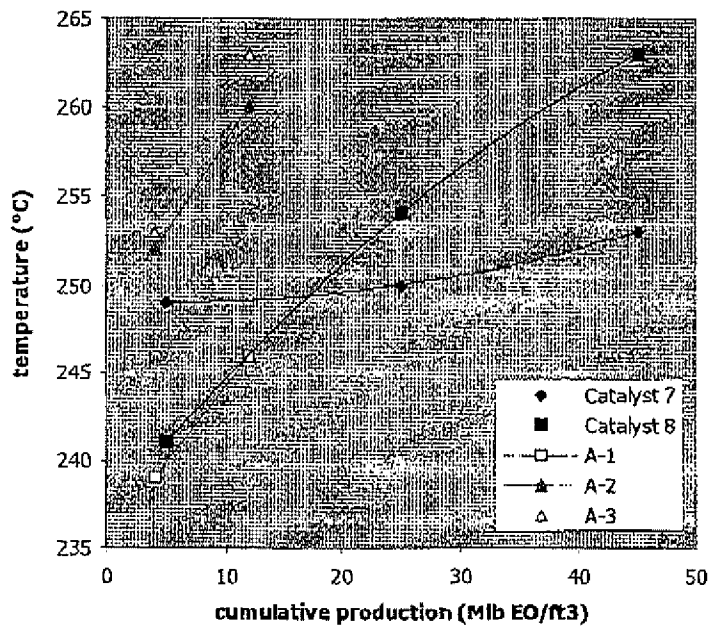
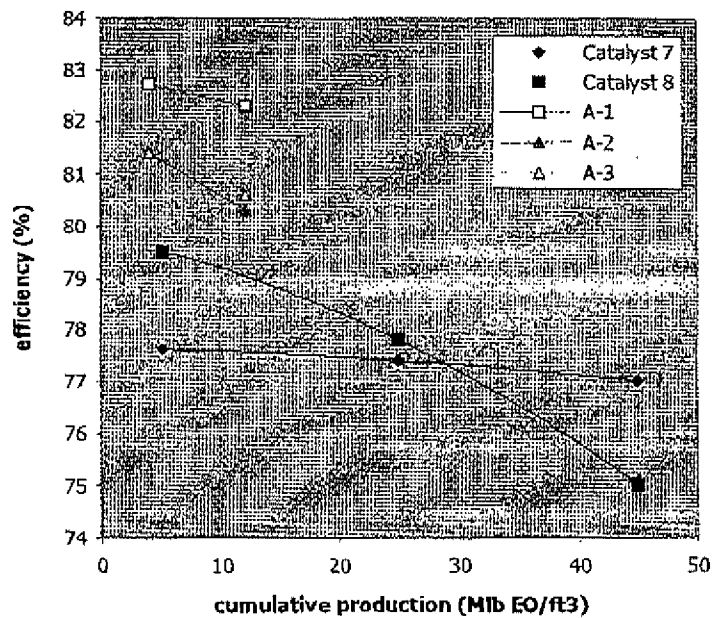


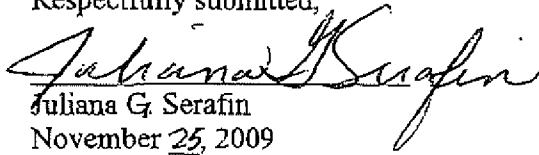
Figure 2 - comparison of efficiency aging rates



23. I declare further that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title

18 of the United States Code, and that willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,


Juliana G. Serafin
November 25, 2009